

AD-759 960

STABILIZATION OF CURE RATES OF DIISOCYANATES WITH HYDROXY-TERMINATED POLY-BUTADIENE BINDERS

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Alabama University

Prepared for:

Army Missile Command

April 1973

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AD 759960

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HYDROXY-TERMINATED POLYBUTADIENE BINDERS

by

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Final Technical Report

This research work was supported by the
U. S. Army Missile Command under
Contract No. DAAH01-72-C-0662

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Huntsville, Alabama

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TABLE OF CONTENTS

	<u>Page</u>
Introduction	1
Kinetics of Model Isocyanate/Alcohol Reactions	2
Results and Discussion of Heterogeneous Catalysts	5
Homogeneous Catalysis Studies	8
Effect of Light on Reaction of Isocyanate/Alcohol Reaction	11
Degradation of Ferrocene Derivatives by AP	20
Degradation of Ferrocene by Air Oxidation	23
Summary and Recommendations	25
References	26

LIST OF TABLES

	<u>Page</u>
TABLE I	6
TABLE II	9
TABLE III	13
TABLE IV	15
TABLE V	17
TABLE VI	19
TABLE VII	24

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
The University of Alabama in Huntsville		Unclassified	
		2b. GROUP	
3. REPORT TITLE			
STABILIZATION OF CURE RATES OF DIISOCYANATES WITH HYDROXY-TERMINATED POLYBUTADIENE BINDERS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Final Technical Report, December 1971 - March 1973			
5. AUTHOR(S) (First name, middle initial, last name)			
Samuel P. McManus, Harold S. Bruner, and H. Dwain Coble			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1973		26	7
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
DAAH01-72-C-0662		UAH Research Report No. 140	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT			
Approved for public release - distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		U. S. Army Missile Command Redstone Arsenal AL 35809	
13. ABSTRACT			
<p>Studies of the effects of various catalysts on the reaction between alkyl isocyanates and alcohols have been carried out. In general, substances soluble in the reactants are more effective catalysts with organoiron derivatives being the most effective of those studied. The reaction was found to be light-assisted and ferrocene was shown to be a catalyst both in the presence of and in the absence of light. Ferrocene and its derivatives are degraded by light in the presence of air and by ammonium perchlorate.</p>			

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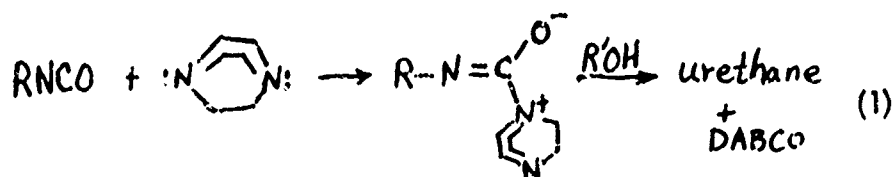
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Introduction

The purpose of this study was to define the catalytic effect of various propellant ingredients or potential additives on the rate of reaction of a model alcohol-isocyanate reaction. The object was to define those species and factors which contribute to a short pot-life in hydroxy-terminated polybutadiene (HTPB) bound propellants and to test various means of sequestering these species or, alternatively, of removing them.

The reaction between an alcohol and an isocyanate, the reaction occurring in the cure process of HTPB propellants, is highly susceptible to both catalytic and steric influences. These factors have been treated in recent reviews.¹ Research in the area continues at a significant pace as evidenced from the flow of publications.²

It has been known for some time that either acidic or basic compounds may catalyze alcohol-isocyanate reactions.¹ Basic compounds supposedly attack at carbon to give an activated intermediate. Of those studied DABCO is one of the best basic catalysts known (See Eq. 1). In the second step of the reaction, the alcohol reacts



with the activated intermediate to displace the DABCO and form the urethane linkage. In the absence of added catalysts, the alcohol or the product (urethane) may act as basic catalysts¹ resulting in kinetics which deviates from true second order. Thus for proper treatment instead of the simple expression:

$$\text{rate} = k [\text{alcohol}] [\text{isocyanate}]$$

the expression for the observed rate, k_t , becomes:

$$k_t = k_o + k_c [\text{catalyst}]$$

where k_o is the rate constant for the uncatalyzed reaction and k_c is rate constant for that portion of the reaction which is catalyzed. Rate measurements are further complicated by an induction period of unknown origin.

Bronsted catalysis is not often used. Organometallic species, however, can be powerful catalysts, and that may be occurring by the organometallic species acting as a Lewis acid. A number of studies have appeared relative to the kinetics of catalysis where organometallic species are involved, but the mechanism of their action is not well known in many cases.¹ There well may be different mechanisms for different organometallic species. Studies of the steric effects operative with ferric acetylacetonate, DABCO, and for the uncatalyzed reaction, definitely indicate a different mechanism for DABCO and $\text{Fe}(\text{acac})_3$.³ The results of Komratova *et al*⁴ and Bruenner and Oberth⁵ are also significant in determining the mechanism of action. A complex mechanism is indicated and apparently the site of involvement with the catalyst is the isocyanate oxygen and not the carbon or nitrogen.³⁻⁵

Kinetics of Model Isocyanate/Alcohol Reactions

As a model reaction to use to study the effects of catalysts on the cure reaction in propellants, we chose *n*-butanol and cyclohexyl isocyanate. The reactants were purified by distillation and stored in a desiccator to prevent uptake of moisture.

A kinetic method was selected which made use of the absorption of the urethane linkage and alcohol group in the near infrared region. Kogan⁶ had reported using the appearance of the urethane absorption as a means of following the kinetics of such reactions. We found that his method was insensitive to the first portion of the reaction. Thus, using observations made by Ortiz,⁷ we decided to use the disappearance of the alcohol as our means of obtaining rate data. Solvents were tested for their suitability and most polar solvents were eliminated because they failed to give a straight baseline. Carbon tetrachloride was chosen as the solvent for our system. In this solvent the n-butanol absorption is at 1.406μ and the system follows Beer's Law.

Initially a number of kinetic runs were made with no added catalyst to determine the desired temperature and concentration. From runs at 50, 65, and 68.5°C , induction periods of 15-35 minutes were observed and an activation energy of 14.95 kcal/mole was calculated for the spontaneous reaction. At 50°C the uncatalyzed reaction was quite slow, but trial runs with iron-containing catalysts showed short reaction times. Thus because of the solvent chosen and the rates likely to be encountered, a temperature of 50°C was selected as standard for our model reaction.

A 10cm jacketed sample cell was constructed out of quartz material. A Haake circulator was used to circulate water through the cell to maintain the temperature at $50.0 \pm 0.5^{\circ}$. Leaving the infrared lamp on for about thirty minutes generates sufficient heat to increase the temperature of the sample by about 2°C . This was not a problem in most runs since the lamp was only on during the measurement of

a kinetic point.

A major effect, casting doubt on the validity of some earlier runs, was observed after the majority of scheduled kinetic runs had been completed. In an attempt to observe the effect of light on ferrocene catalysis, some runs were made with ferrocene with the lamp off. All previous runs had been made with the lamp continuously on since ferrocene reactions were generally complete in less than a half-hour. The difference in light-on and light-off rates was indeed significant. The specific results will be discussed later at an appropriate time. The result of those studies, however, led us to discover that the basic isocyanate reaction can be photo-catalyzed by ultraviolet light. We were somewhat surprised to learn that the near-ir source emitted significant amounts of uv light and that the isocyanate reacted differently under the influence of light. This, thus, affects all data to some extent, with the exception of those runs made using light filters. Since oxygen is a retarder for the light-assisted process and since most reactions were not run with continuous light, most data is still valid. For example, the light-assisted process does not affect any of the heterogeneous systems since they were all run in a different reaction pot as described below.

The cell described above was not appropriate for use with those materials found to be insoluble in carbon tetrachloride. Thus, a new process was designed. A 1000 ml reaction flask was fitted with an efficient stirrer and a septum for extracting samples. The system was charged with the reactants, flushed with N_2 , and stirred immersed in a bath at $50.0^{\circ}C$.

For any reaction, homogeneous or heterogeneous, where a very slow reaction was

observed by the near ir method, the method was checked by gas chromatography to see that both alcohol and isocyanate still remained unreacted. This precaution prevents the misinterpretation of results since isocyanates are known to undergo dimerization processes. The unreacted cyclohexyl isocyanate is easily observed by gas chromatography.

The data presented here normally represents at least duplicate runs. In some cases the average of several runs is included.

Results and Discussion of Heterogeneous Catalysts

The results of kinetic studies employing heterogeneous catalysts are shown in Table I. From the relative rate data, it is observed that one gram of 200 μ AP is more catalytic than an equal quantity of freshly ground 3 μ AP. Increasing the quantity of 200 μ also causes a rate increase up to about 15 grams where stability is approached. It cannot be argued that our results confirms that an increase in surface area is the reason for the increase, since the 3 μ AP should have been faster than 200 μ AP. Perhaps the AP was prepared differently causing a different effect. Alternatively, the data can be explained by the presence of some acidic present in the AP, possibly perchloric acid, which acts as an acid catalyst for the reaction. Regardless of the reasons, A² appears to be a rate acceleration.

When coated, AP acts differently. TCP, which is a rate retarder, does not significantly affect the rate when used as a coating on AP. Alon C, which is a mild retarder, also produces a retarding effect in Alon C coated AP. Upon increasing the amount of Alon C coated AP, the large rate increase is somewhat suppressed.

TABLE I. Second Order Rate Constants for the Heterogeneous Catalyzed Reactions of 0.1M Cyclohexyl Isocyanate with 0.1M n-Butyl Alcohol in Carbon Tetrachloride at 50°.

Catalyst	Weight Used (gm)	Particle Size (u)	Observed Rate (liter/mole-sec)	Relative Rate
None			4.67×10^{-5}	1.00
AP	1	3	6.87×10^{-5}	1.47
AP	0.5	200	1.67×10^{-4}	3.58
AP	1	200	2.10×10^{-4}	4.50
AP	2	200	7.25×10^{-4}	15.52
AP	5	200	1.06×10^{-3}	22.70
AP	10	200	1.14×10^{-3}	24.41
AP	15	200	8.03×10^{-4}	17.19
AP coated with TCP	1	3	4.44×10^{-5}	0.95
AP coated with TCP	1	16	6.94×10^{-5}	1.49
AP control with phenethylaziridine	1	1	6.10×10^{-5}	1.31
AP coated with Alon C	1	2.5	4.22×10^{-6}	0.09
AP coated with Alon C 10		2.5	6.17×10^{-6}	1.32
Alon C	0.1		2.08×10^{-6}	0.45
TCP	1		5.97×10^{-6}	0.13

TABLE I. Continued:

Catalyst	Weight Used (gm)	Particle Size (μ)	Observed Rate (Liter/mole-sec)	Relative Rate
FeO ₃ as received ^a	1		5.05×10^{-4}	1.08
FeO ₃ calcined ^a	1		3.00×10^{-4}	0.64
FeO ₃ calcined ^b	1		1.60×10^{-4}	0.43
Al H5	1		3.89×10^{-4}	0.83
Al H10	1		6.43×10^{-4}	1.38
Al H60	1		8.94×10^{-4}	1.91
Al 230	1		5.32×10^{-4}	1.14
Alcoa Al-5214 Lot ¹⁰¹⁰	1		4.27×10^{-4}	0.91
Alcoa Al-5159 Lot ¹⁰¹¹	1		5.22×10^{-4}	1.12
Al-Alcan X-75-1 Lot 152	1		3.86×10^{-4}	0.83
Reynolds Al 5392 Lot 9912	1		9.23×10^{-4}	1.98

a) Reaction time < 12 hr.

b) Reaction time > 12 hr.

Aluminum and iron oxide samples gave most unusual rate data. With most grades of aluminum, the reaction rate was close to that of the uncatalyzed reaction until, after some unpredictable time interval, an extremely high rate would occur for a brief period after which the rate would return to the earlier, slower level. With the same grade of aluminum, this higher rate might appear within an hour of mixing or might not appear during the entire 12 hour kinetic run. Due to the unpredictable nature of these rapid rates, accurate kinetic data could not be obtained and therefore, the rates reported are those observed during the slower periods. The iron oxide "as received" displayed a constant rate after a short induction period, but the calcined sample behaved in a manner similar to the aluminum catalysts except that the rate enhancement was not as large and the time interval (before rapid reaction began) was much longer with the iron oxide sample. The effect is not really understood, but may be caused by the exposure of catalytic sites on the metal surface by the action of the reactants or by the stirrer. Rapid reaction would occur until the catalytic sites were again deactivated.

Homogeneous Catalysis Studies

A number of potential propellant additives were tested for catalytic activity in the model isocyanate/alcohol reaction. In this section, those which were soluble in CCl_4 are treated. The data in Table II lists the average rates for several compounds or mixtures. Of interest is the fast rate shown by iron-containing compounds and the slow rate by MAPO and MT-4 and the lack of reaction with tetramethylthiuram disulfide present. Most of the other compounds were more or less non-catalytic. The ferrocene compounds are acting as catalysts for the photo-assisted reaction, discussed later, as well as catalysts for the ionic reaction. $\text{Fe}(\text{acac})_3$ only catalyzes the ionic

TABLE II.

Second Order Rate Constants for the Homogeneous Catalyzed Reactions of Cyclohexyl
Isocyanate with 1-Butanol in CCl_4 at 50°C

Catalyst	Conc. of Cat. (M)	Conc of Reactants (-NCO) = $-\ddot{\text{O}}\text{H}$ (M) $\times 10^{-2}$	Ave. Obs Rate liter/mole- sec.	Ave Rel. Rate	Remarks
Name					
Ferrocene (Me_2NCS) ₂	3.22×10^{-4}	5.00	2×10^{-4}	1.00	a, b
(Me_2NCS) ₂	1.18×10^{-4}	4.86	1.30×10^{-2}	65	No reac after 3 days.
(Me_2NCS) ₂	3.22×10^{-4}	4.41	0	0	
TOPO	3.12×10^{-4}	4.86	3.52×10^{-4}	1.76	
Catocene, as rec'd.	3.22×10^{-4}	4.86	4.17×10^{-4}	2.09	
Catocene, deionized	3.22×10^{-4}	4.86	9.60×10^{-3}	48	b, some insol. matl. present
Catocene, deionized + 1% Hydroquinone	3.22×10^{-4}	4.86	8.49×10^{-3}	42	b, Cat. used unmed. upon prep.
FeCl_3	3.22×10^{-4}	4.86	9.02×10^{-3}	45	b
n-Butyl ferrocene	3.2×10^{-4}	4.86	4.00×10^{-3}	20	b, freshly prep.
Diethyl adipate	3.2×10^{-4}	4.86	8.32×10^{-3}	41.6	b
Diisocetyl pelargonate	3.2×10^{-4}	4.86	3.05×10^{-4}	1.52	
n-Hexyl Carborane	3.2×10^{-4}	4.86	3.00×10^{-4}	1.50	
			2.20×10^{-4}	1.05	

TABLE II. Continued

Catalyst	Conc. of Cat. (M)	Conc of Reactants (-NCO = -)H) (M) $\times 10^2$	Ave. Obs. Rate liter/mole-sec.	Ave Rel. Rate	Remarks
MT-4	3.2×10^{-4}	4.86	1.40×10^{-3}	0.07	
Fe(acac) ₃	3.2×10^{-4}	4.86	4.16×10^{-2}	182	b
C ₄ H ₉ Fe(CO) ₅	3.2×10^{-4}	4.86	2.48×10^{-2}	124	b
Ca ₃ (PO ₄) ₂ , TCP	3.2×10^{-4}	4.86	7.5×10^{-4}	3.75	Soln turbid
Cu Br ₂	3.2×10^{-4}	4.86	4.16×10^{-4}	2.08	2 phase soln
Pb(C ₂ H ₃ O ₂) ₄	3.2×10^{-4}	4.86	2.5×10^{-4}	1.24	
MAPO	3.2×10^{-4}	4.86	2.2×10^{-5}	0.11	
(C ₄ H ₉) ₃ NO, tributyl amine oxide	3.2×10^{-4}	4.86	2.4×10^{-4}	1.1	
Dibutyl Sulfone	3.2×10^{-4}	4.86	2.4×10^{-4}	1.1	

^aFerrocene is double sublimed, but no precautions were taken to protect it from light.

^bLight on throughout reaction.

reaction, thus its effect shown here is real. Catacene is not as good a catalyst as ferrocene.

Several synergistic catalyst studies were run to determine if certain compounds could act as sequestering agents for the good catalysts. These data are summarized in Tables III and IV. Ferric chloride activity is significantly reduced by a number of additives probably by complexation of the ferric ion, and ferrocene is sequestered best by thiuram derivatives. The tetrabutyl derivative was synthesized and tested since it is a liquid while the tetramethyl derivative is a solid.

Effect of Light on Reaction of Isocyanate/Alcohol Reaction

As mentioned earlier, the isocyanate/alcohol reaction was found to be catalyzed by light. Through the use of certain additives and the use of optical filters, the process was found to be one possibly involving the formation of a triplet isocyanate. This process should not occur in rocket motor curing. Both ferrocene and benzophenone are known photosensitizers, but only ferrocene speeds the rate of the photoreaction possibly because insufficient light exists at higher energy to excite benzophenone. Use of filters showed that ferrocene was still a catalyst in the absence of light. The 650 filter (Table V) cuts out all light that ferrocene absorbs in its electronic spectrum, but allows the near IR light to pass. Without light catalysis, ferrocene still catalyzes the reaction so that it occurs about 30 times faster than the uncatalyzed reaction. When ferrocene was exposed to light for thirty minutes prior to its addition and the reaction was run without uv light present, it was a better catalyst. Thus light should be excluded from ferrocene at all stages of its handling. Catacene is not as susceptible to light activation as ferrocene (compare 650 filter run vs. no

filter in Table V). Without light, however, catocene, freshly purified, still makes the reaction go 10 times faster than the uncatalyzed reaction. Table VI shows the effect of concentration of ferrocene on the light-assisted process. Note that without a nitrogen atmosphere, the reaction is slower. This is due to oxygen retarding the photo-assisted process.

TABLE III. Second Order Rate Constants for the Homogeneous Catalyzed Reactions of Cyclohexyl Isocyanate with 1-Butanol in CCl_4 at 50°C .

Catalyst Combination (ratio)	Conc. of Catalyst (s) (M)	Conc. of Reactants ($-\text{NCO} = -\text{OH}$) ($\text{M} \times 10^{-3}$)	Ave. Obs. Rate liter/mole-sec.	Rel. Rate	Remarks
None	-	5.00	2×10^{-4}	1	
Ferrocene + MAPO (1:1)	3.12×10^{-4}	4.68	1.01×10^{-2}	50.5	a, b
FeCl_3 + MAPO (1:1)	3.12×10^{-4}	4.68	3.4×10^{-4}	1.7	c
FeCl_3 + $(\text{C}_4\text{H}_9)_3\text{NO}$ (1:1)	3.12×10^{-4}	4.68	9.8×10^{-4}	4.9	c
FeCl_3 + Dithiooxamide (1:1)	3.12×10^{-4}	4.68	5.8×10^{-4}	2.9	c
FeCl_3 + Sodium diethyl Dithiocarbamate (1:1)	3.12×10^{-4}	4.68	8.4×10^{-4}	4.2	c
FeCl_3 + TOPO (1:1)	3.12×10^{-4}	4.68	1.48×10^{-3}	7.4	c
FeCl_3 + Tributyl Phosphine Oxide (TBPO) (1:1)	3.12×10^{-4}	4.68	2.30×10^{-3}	11.5	c
FeCl_3 + Sodium diethyl Dithiocarbamate (1:4)	2.85×10^{-4} 11.4×10^{-4}	4.28	1.25×10^{-3}	0.62	c

TABLE III. Continued

Catalyst Combination (Ratio)	Conc. of Catalyst (s) (M)	Conc. of Reactants (-NCO = $\bar{\text{O}}\text{H}$) (M $\times 10^{-2}$)	Ave. Obs. Rate liter/mole-sec.	Rel. Rate	Remarks
$\text{FeCl}_3 + \text{TOPO}$ (1:5)	2.77×10^{-4} 13.85×10^{-4}	4.16	1.72×10^{-3}	8.6	c
$\text{FeCl}_3 + (\text{Me}_2\text{NCS})_2$ (1:1)	3.12×10^{-4}	4.68	7.03×10^{-4}	3.52	c,d
Ferrocene + $(\text{Me}_2\text{NCS})_2$ (1:1)	3.12×10^{-4}	4.68	7.33×10^{-4}	37	a,b,d
Ferrocene + $(\text{Me}_2\text{NCS})_2$ (1:4)	2.85×10^{-4} 11.4×10^{-4}	4.28	1.84×10^{-4}	0.92	a,d

^a Ferrocene is double sublimed, but no precautions were taken to protect it from light.
^b Light on throughout reaction.

^c FeCl_3 was freshly prepared and handled in a dry box. In some cases the FeCl_3 was first dissolved in acetone.
^d $(\text{Me}_2\text{NCS})_2$ is tetramethyl thiouramdisulfide.

TABLE IV. Second Order Rate Constants for the Homogeneous Catalyzed Reaction of Cyclohexyl Isocyanate with n-Butyl Alcohol in CCl_4 at 50° a Nitrogen Atmosphere.

Catalyst	Conc ⁿ of Catalyst (s) (M)	Conc ⁿ of Reactants (-NCO = -OH) (M x 10 ⁻²)	Observed Rate (liter/mole-sec.)	Relative Rate to Corresponding Reaction	Remarks
None		5.00	5.42×10^{-4}	1.00	Light on during reaction.
None		5.00	2.08×10^{-4}	1.00	Light off except to scan.
Ferrocene	3.22×10^{-4}	4.86	8.30×10^{-4}	15.3	Light on during reaction.
Ferrocene 1,3 - pentadiene (1:1)	3.17×10^{-4}	4.76	8.22×10^{-4}	15.2	Light on during reaction.
Ferrocene + (Bu ₂ NCS) ₂ (1:1)	3.12×10^{-4}	4.86	.123	22.7	Light on during reaction.
Ferrocene + (Bu ₂ NCS) ₂ (1:2)	3.03×10^{-4} 6.06×10^{-4}	4.55	1.14×10^{-2}	2.10	Light on during reaction.

TABLE IV. Continued

Catalyst	Conc ⁿ of Catalyst (M)	Conc ⁿ of Reactants (-NCO = -OH) (M x 10 ⁻³)	Observed Rate (Liter/mole-sec.)	Relative Rate to Corresponding Reaction	Remarks
Ferrocene + (Bu ₂ NCS) ₂ (1:4)	2.86 x 10 ⁻³ 1.43 x 10 ⁻³	4.27	8.50 x 10 ⁻⁴	0.16	Light on during reaction.
(Bu ₂ NCS) ₂	3.22 x 10 ⁻³	4.86	2.14 x 10 ⁻³	0.39	Light on during reaction.
(Bu ₂ NCS) ₂	3.22 x 10 ⁻³	4.86	7.83 x 10 ⁻⁴	0.38	Light off except to scan.
(Bu ₂ NCS) ₂	1.18 x 10 ⁻³	4.41	2.53 x 10 ⁻⁴	0.012	Light off except to scan.

TABLE V. Effect of Light on the Activity of Homogeneous Catalysts for the Reaction of Cyclohexyl Isocyanate with n-Butyl Alcohol in Carbon Tetrachloride at 50°C.

Catalyst ^(a)	Conc. of Catalyst (M)	Conc of Reactants (-NCO=O) (M) x 10 ³	Long Pass Optical Filter Used	Rate of Constant (liter/mole-sec.)	Remarks
None		5.90	None	5.42×10^{-3}	Light on for entire run.
None		5.00	None	2.08×10^{-4}	Light off except to scan.
Benzophenone	.12	4.41	None	5.22×10^{-3}	Nitrogen atmosphere
Benzophenone	.12	4.41	650	5.28×10^{-5}	Nitrogen atmosphere
Benzophenone	.016	4.92	None	7.35×10^{-3}	Nitrogen atmosphere
Ferrocene	3.22×10^{-4}	4.86	None	4.33×10^{-3}	
Ferrocene	3.22×10^{-4}	4.86	400	2.58×10^{-3}	
Ferrocene	3.22×10^{-4}	4.86	450	8.37×10^{-3}	
Ferrocene	3.22×10^{-4}	4.86	650	6.37×10^{-3}	
Ferrocene	3.22×10^{-4}	4.86	650	1.20×10^{-3}	Ferrocene irradiated without filters for 30 min. before addition of other reagents.

TABLE V. Continued.

Catalyst (a)	Conc. of Catalyst (M)	Conc of Reactants (-NCO=OH) (M) $\times 10^2$	Long Pass Optical Filter Used	Rate of Constant (liter/mole-sec.)	Remarks
Catocene	3.22×10^{-4}	4.86	None	8.49×10^{-3}	
Catocene	3.22×10^{-4}	4.86	450	9.42×10^{-3}	
Catocene	3.22×10^{-4}	4.86	650	2.08×10^{-3}	
$\text{Fe}(\text{CO})_4(\text{C}_4\text{H}_6)$	3.22×10^{-4}	4.86	None	6.50×10^{-2}	
$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_6)$	3.22×10^{-4}	4.86	450	5.00×10^{-2}	
$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_6)$	3.22×10^{-4}	4.86	650	8.87×10^{-2}	

(a) All catalyst solutions prepared in darkened room.

TABLE VI. Effect of Changes in Ferrocene Concentration on the Rate of Reaction of Cyclohexyl Isocyanate with n-Butyl Alcohol at 55° in CCl_4

Conc ⁿ of Ferrocene ($\text{M} \times 10^{-5}$)	Conc ⁿ of Reagents (-NCO = -OH) ($\text{M} \times 10^{-2}$)	Rate Constants (liter/mole-sec)	Remarks
1600	4.84	1.83×10^{-2}	nitrogen atmosphere
644	4.29	2.18×10^{-2}	
322	4.84	3.54×10^{-2}	
322	4.84	8.30×10^{-2}	
161	4.29	2.65×10^{-2}	
32.2	4.84	2.96×10^{-2}	nitrogen atmosphere
16.1	4.29	1.16×10^{-2}	
3.22	4.84	3.33×10^{-3}	
16.1	4.29	.219	
3.22	4.84	5.40×10^{-2}	

Degradation of Ferrocene Derivatives by AP

The possibility exists that the oxidation reaction that undoubtedly occurs in the fuel mixture between the catocene and the large excess of ammonium perchlorate might form a better catalyst for the cure reaction than had previously existed. The oxidation products from the ferrocene derivative might include only a ferricinium derivative (Fe(II) to Fe(III) oxidation), or might involve oxidation of the ring positions or formation of decomposition products from the Fe(III) compound. The product of the reduction of the perchlorate might also prove a more active catalyst than the perchlorate.

In order to investigate the oxidation reaction, one mole of uncoated, finely ground (3 μ) ammonium perchlorate was suspended under nitrogen at 55° for 10 days in each of the following solutions: 0.1 mole of sublimed ferrocene in CCl₄, 0.1 mole of deionized catocene in CCl₄, 0.1 mole of sublimed ferrocene in xylene and 0.1 mole of sublimed ferrocene in CCl₄ that was 0.2M in n-butanol. In each case, dark blue-green precipitates formed, indicative of ferricinium salts, but the degradation was less complete in the reaction containing butanol and still less complete in the reaction in xylene. The solvent was removed under vacuum from representative aliquots of each reaction, and the residues were studied by NMR, and IR and visible spectroscopy. The 90 MHz NMR spectra in d₆-acetone of the residues from the degradations in xylene and in butanol-CCl₄ showed considerable broadening of the one band in the ferrocene spectrum, but no new peaks were observed. The broadening was attributed to the formation of the paramagnetic ferricinium complex. Extensive paramagnetic effects prevented NMR spectra from being obtained for the

other two samples. The nujol-mull infrared spectra were badly obscured by the large excess of AP present in the residues, but some undegraded metallocene could be observed in each product. The visible spectrum of the residue of the degradation of ferrocene (by AP in CCl_4) in water showed the same absorption maximum (at 6170Å) as an independently synthesized sample of ferricinium perchlorate.

Since the degradations were run before the light sensitivity of ferrocene was completely understood, all the above reactions were run on the desk top under normal laboratory lighting. To make certain that the ferrocene degradations could be caused by ammonium perchlorate in the absence of light, the degradation of ferrocene in CCl_4 by AP was repeated in a flask covered with aluminum foil. The degradation occurred at approximately the same rate.

All metallocene degradation products were then investigated as heterogeneous catalysts. The results are summarized in Table VII. To provide a basis for comparison, samples of ferrocene and ferrocene or catocene plus AP which had not previously been subjected to degradation conditions were also studied. Although the variation in rate constant was not large, the more extensively degraded samples display slightly less catalytic activity. This lessened activity is presumably the result of the limited solubility of metallocinium ion in the reaction medium. These heterogeneous catalytic reactions were also run before the light sensitivity of ferrocene catalysis was known, but all were run under equivalent lighting conditions. It appears from this study that ferrocene (or catocene) will readily be

oxidized to the ferricinium ion by insoluble AP in a nonpolar medium, such as HTPB. Toward the cure reaction, however, the resultant compounds, have about the same catalytic activity as had the starting materials.

Degradation of Ferrocene by Air Oxidation

Throughout this study it was noted that ferrocene and its derivatives showed variable rates when old solutions or old samples were used. Although ferrocene is easily purified, it is easily oxidized by oxygen. Solutions prepared in carbon tetrachloride begin to collect a solid residue after standing in a lighted room for a few hours. In one experiment we exposed a carbon tetrachloride solution of ferrocene to the near ir source light without taking precautions to eliminate air. After thirty minutes, a precipitate had formed in the cell and a scan of the visible spectrum indicated that ferricinium ion was present. Thus, uv light and oxygen are apparently photooxidizing the ferrocene. In later kinetic runs, oxygen was excluded to prevent this mode of degradation.

TABLE VII. Second Order Rate Constants for the Reaction of .1M Cyclohexyl Isocyanate with .1M n-Butyl Alcohol in CCl_4 at 50° Employing Metallocene and Ammonium Perchlorate Catalysts

Metallocene	Wt. Used (g)	Wt. AP (g)	No. of Runs	(liter/mole-sec)	Remarks
Ferrocene	.126	0	2	6.05×10^{-3}	
Ferrocene	.126	.874	2	6.73×10^{-3}	
Ferrocene	.126	.874	2	6.07×10^{-3}	Catalyst recovered from degrad. at 55° in toluene for 10 days.
Ferrocene	.126	.874	2	4.04×10^{-3}	Catalyst recovered from degrad. at 55° in .2M BuOH in CCl_4 for 10 days.
Ferrocene	.126	.874	2	5.00×10^{-3}	Catalyst recovered from degrad. at 55° in CCl_4 for 10 days.
Catocene	.256	.744	2	3.04×10^{-3}	
Catocene	.256	.744	2	1.15×10^{-3}	Catalyst recovered from degrad. at 55° CCl_4 for 10 days.

Summary and Recommendations

A large number of kinetic measurements have been made on a model isocyanate/alcohol reaction to determine the effect that the catalysts may have on the HTPB propellant pot life. It was determined that AP is catalytic but that the effect appears to be other than of a surface effect. It could be impurities such as a small amount of perchloric acid, metallic impurities from its preparation, or some unknown impurity of another nature. Iron-containing compounds are generally active catalysts. The specific activity is due to the state of purity and history of the sample. Ferrocene derivatives are especially susceptible to degradation in the presence of light and are highly catalytic when exposed to light. $\text{Fe}(\text{acac})_3$ is fairly stable and its catalytic activity is not affected by light.

We recommend that some attention be given to the further investigation of how AP acts as a catalyst. We further recommend that any ferrocene derivatives used should be subject to purification by deionization prior to use. After purification they should be stored under nitrogen in the dark and not exposed to air or light during mixing if possible.

Some of the better sequestering agents, for example, some mixtures containing MAPO, some thiourea derivatives, and some AP coating agents should be carefully screened in small motor processing to measure the effect of pot-life in actual motor mixes. Coatings for iron oxide may also improve pot-life since that species seems to act unpredictably as a catalyst.

We are further investigating the photoassisted reaction aside from this study since its mechanism is intriguing.

References

1. (a) K. C. Frisch in *Polyurethane Technology*, ed. by P. F. Bruins, Wiley, New York, 1969 pp. 1-38; (b) K. C. Frisch and L. P. Lomas, *Rev. Macromol. Chem.*, 6, 103 (1971); (c) A. Petrus, *St. cerc. chim.*, 18, 1089 (1970).
2. The following Chem. Abst. references are appropriate additions to Ref. 1; CA, 73, 120973; CA, 75, 156969; CA, 75, 62718; CA, 69, 45024; CA, 70, 107054; CA, 72, 112293; CA, 74, 41590; and CA, 67, 21224.
3. S. P. McManus, H. S. Bruner, and M. Ortiz, unpublished results.
4. V. V. Komratova, et. al., *Kinetika i Kataliz*, 11, 1406 (1970).
5. R. S. Bruerner and A. E. Oberth, *J. Org. Chem*, 31, 887 (1966).
6. I. C. Kogan, *ibid.*, 24, 438 (1959).
7. M. Ortiz, unpublished results, to be incorporated in a M.S. Thesis, University of Alabama in Huntsville, 1973.